

PCT

WORLD INTELLECTUAL
PROPERTY ORGANIZATION

INTERNATIONAL APPLICATION PUBLISHED

WO 9602924A1

(51) International Patent Classification 6 :

H01C 7/10

A1

(43) International Publication Date:

1 February 1996 (01.02.96)

(21) International Application Number: PCT/US95/08808

(22) International Filing Date: 14 July 1995 (14.07.95)

(30) Priority Data:
08/275,154 14 July 1994 (14.07.94) US

(71) Applicant (for all designated States except US): ORYX TECHNOLOGY CORPORATION [US/US]; 47341 Bayside Parkway, Fremont, CA 94538 (US).

(72) Inventors; and

(75) Inventors/Applicants (for US only): SHRIER, Karen, P. [US/US]; 42986 Noria Road, Fremont, CA 94539 (US). BEHLING, Gerald, R. [US/US]; 15109 Nob Hill Drive, San Jose, CA 95127 (US). INTRATER, James, B. [US/US]; 592 Mill Creek Lane #316, Santa Clara, CA 95054 (US). JOSHI, Kailash, C. [US/US]; 1593 Pebble Beach Court, Milpitas, CA 95117 (US). ALSTON, William, W., Jr. [US/US]; 1024 Thistle Court, Sunnyvale, CA 94086 (US).

(74) Agent: DILLAHUNTY, T., Gene; Burns, Doane, Swecker & Mathis, P.O. Box 1404, Alexandria, VA 22313-1404 (US).

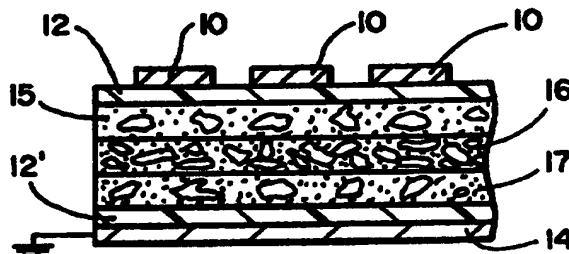
(81) Designated States: AM, AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LT, LU, LV, MD, MG, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG), ARIPO patent (KE, MW, SD, SZ, UG).

Published

With international search report.

Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.

(54) Title: SINGLE AND MULTI-LAYER VARIABLE VOLTAGE PROTECTION DEVICES AND METHODS OF MAKING SAME



(57) Abstract

Disclosed is a variable voltage protection device for electronic devices which in one aspect comprises a thin layer of neat dielectric polymer, glass or ceramic (12) positioned between a ground plane (14) and an electrical conductor (10) for overvoltage protection, wherein the neat polymer, glass or ceramic layer does not include the presence of conductive or semiconductive particles. Also disclosed is the combination of the neat dielectric polymer, glass or ceramic thin layer (12) positioned on a conventional variable voltage protection material (13) comprising a binder containing conductive, semiconductive or insulative particles. A multi-layer variable voltage protection component is disclosed comprising three layers of overvoltage protection material (15, 16, 17) wherein the outer two layers contain a lower percentage of conductive, semiconductive and/or insulative particles and wherein the inner layer contains a higher percentage of conductive, semiconductive and/or insulative particles. The multi-layer component can optionally be used in combination with the neat dielectric polymer, glass or ceramic layer (12, 12') and can optionally have interposed metal layers (18, 18'). A method is disclosed for dispersing colloidal insulative particles and conductive, semiconductive and/or insulative particles using a volatile solvent for dispersement of the colloidal insulative particles and the conductive, semiconductive or insulative particles before mixing the resultant particles with the binder.

BEST AVAILABLE COPY

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	GB	United Kingdom	MR	Mauritania
AU	Australia	GE	Georgia	MW	Malawi
BB	Barbados	GN	Guinea	NE	Niger
BE	Belgium	GR	Greece	NL	Netherlands
BF	Burkina Faso	HU	Hungary	NO	Norway
BG	Bulgaria	IE	Ireland	NZ	New Zealand
BJ	Benin	IT	Italy	PL	Poland
BR	Brazil	JP	Japan	PT	Portugal
BY	Belarus	KE	Kenya	RO	Romania
CA	Canada	KG	Kyrgyzstan	RU	Russian Federation
CF	Central African Republic	KP	Democratic People's Republic of Korea	SD	Sudan
CG	Congo	KR	Republic of Korea	SE	Sweden
CH	Switzerland	KZ	Kazakhstan	SI	Slovenia
CI	Côte d'Ivoire	LI	Liechtenstein	SK	Slovakia
CM	Cameroon	LV	Latvia	SN	Senegal
CN	China	MC	Monaco	TD	Chad
CS	Czechoslovakia	MD	Republic of Moldova	TG	Togo
CZ	Czech Republic	MG	Madagascar	TJ	Tajikistan
DE	Germany	ML	Mali	TT	Trinidad and Tobago
DK	Denmark	MN	Mongolia	UA	Ukraine
ES	Spain			US	United States of America
FI	Finland			UZ	Uzbekistan
FR	France			VN	Viet Nam
GA	Gabon				

**SINGLE AND MULTI-LAYER
VARIABLE VOLTAGE PROTECTION DEVICES AND
METHODS OF MAKING SAME**

Field of the Invention

5 The present invention relates generally to variable voltage protection devices used to protect electronic circuits from overvoltage transients caused by lightning, electromagnetic pulses, electrostatic discharges, ground loop induced transients, or inductive power surges. The present invention relates particularly to materials of construction
10 for variable voltage protection components and methods of making variable voltage protection components and devices.

Background of the Invention

 Voltage transients can induce very high currents and voltages that can penetrate electrical devices and damage them, either causing
15 hardware damage, such as semiconductor burnout, or electronic upset, such as transmission loss or loss of stored data. The voltage transients produce large voltage spikes with high peak currents (i.e., overvoltage). The three basic overvoltage threats are electrostatic discharge, line transients, and lightning. Electrostatic discharge
20 typically occurs when static charge dissipates off the body of a person in direct physical contact with an operating electronic system or an individual component, such as an integrated circuit chip. Line transients are surges in AC power lines. Line transients can also occur due to closing a switch or starting a motor. Lightning strikes can strike
25 stationary objects, such as a building, or mobile objects such as aircraft or cellular phones. Such strikes can suddenly overload a system's electronics. At peak power, each of these threats is capable of destroying the sensitive structure of an integrated circuit chip.

 Various overvoltage protection materials have been used
30 previously. These materials are also known as nonlinear resistance

-2-

materials and are herein referred to as voltage variable materials. In operation, the voltage variable material initially has high electrical resistance. When the circuit experiences an overvoltage spike, the voltage variable material quickly changes to a low electrical resistance state in order to short the overvoltage to a ground. After the overvoltage has passed, the material immediately reverts back to a high electrical resistance state. The key operational parameters of the voltage variable material are the response time, the clamp voltage, the voltage peak and peak power. The time it takes for the voltage variable material to switch from insulating to conducting is the response time. The voltage at which the voltage variable material limits the voltage surge is called the clamp voltage. In other words, after the material switches to conducting, the material ensures that the integrated circuit chip, for example, will not be subjected to a voltage greater than the clamp voltage. The voltage at which the voltage variable material will switch (under surge conditions) from insulating to conducting is the switch voltage. These materials typically comprise finely divided conductive or semiconductive particles dispersed in an organic resin or other insulating medium. For example, U.S. Patent No. 3,685,026 (Wakabayashi, et al.), U.S. Patent No. 4,977,357 (Shrier) and U.S. Patent No. 4,726,991 (Hyatt et al.) disclose such materials.

Voltage variable materials and components containing voltage variable materials have been incorporated into overvoltage protection devices in a number of ways. For example, U.S. Patent No. 5,142,263 and 5,189,387 (both issued to Childers et al.) disclose a surface mount device which includes a pair of conductive sheets and voltage variable material disposed between the pair of conductive sheets. U.S. Patent No. 4,928,199 (Diaz et al.) discloses an integrated circuit chip package which comprises a lead frame, an integrated circuit chip protected by an electrode cover which is connected to ground on one side, and a variable voltage switching device including

-3-

the voltage variable material connected to the electrode cover on the other side. U.S. Patent No. 5,246,388 (Collins et al.) is directed to a device having a first set of electrical contacts that interconnect with signal contacts of an electrical connector, a second set of contacts
5 that connect to a ground, and a rigid plastic housing holding the first and second set of contacts so that there is a precise spacing gap to be filled with the overvoltage material. U.S. Patent No. 5,248,517 (Shrier et al.) discloses painting or printing the voltage variable material onto a substrate so that conformal coating with voltage variable material of
10 large areas and intricate surfaces can be achieved. By directly printing the voltage variable material onto a substrate, the voltage variable material functions as a discreet device or as part of associated circuitry.

The above U.S. Patents referred to are incorporated herein by
15 reference.

Although the prior art discloses various materials and devices, there is a continuing and long felt need to provide improved cost-effective voltage variable materials and devices of more consistent performance properties to prevent variations in the clamp voltage under
20 various conditions in which the materials and devices are used.

Summary of the Invention

This invention comprises in one aspect a variable voltage protection device which comprises a single layer of neat dielectric polymer, glass or ceramic positioned between a ground plane and an
25 electrical conductor of an electronic device. It has surprisingly been found that overvoltage protection can be effectively provided by such a polymer, glass or ceramic layer, provided that the polymer, glass or ceramic layer is sufficiently thin to provide the switching and the voltage clamping characteristics desired for a given protective device
30 for a given electronic device. It has been found that for certain

-4-

polymers the thickness must be less than about 0.0406 mm (1.6 mils) and for other polymers the thickness must be less than about 0.0203 mm (0.8 mil), preferably less than about 0.0127 mm (0.5 mil) and more preferably less than about 0.0051 mm (0.2 mil). For certain

5 glasses and ceramics the thickness must be less than about 0.127 mm (5 mils), preferably less than about 0.0965 mm (3.8 mils) and more preferably less than about 0.0406 mm (1.6 mils), with thicknesses less than 0.0203 mm (0.8 mil) preferred in many applications.

In another aspect of the present invention, superior performance

10 can be provided by a variable voltage protection component which comprises the combination of (a) a layer of variable voltage protection material comprising a binder containing conductive particles and/or semiconductive particles; and (b) a layer of neat dielectric polymer, glass or ceramic in contact with one surface of said layer of variable

15 voltage material; wherein the neat dielectric polymer, glass or ceramic layer is present in a thickness of less than about 0.0406 mm (1.6 mils). The presence of the thin layer of neat dielectric polymer, glass or ceramic on the surface of the binder/particle type of variable voltage protection material provides a component having desirable voltage

20 clamping properties, as well as other desirable properties.

In another aspect, this invention provides a layered variable voltage protection component comprising a first layer of variable voltage protection material comprising a binder having dispersed therein at least about 20% by volume of conductive or semiconductive

25 particles; a second layer of variable voltage protection material in contact with the first layer comprising a binder having dispersed therein at least 40% by volume of conductive or semiconductive particles; and a third layer of variable voltage protection material in contact with said second layer comprising a binder having dispersed

30 therein at least 20% by volume of conductive or semiconductive particles. It has been found that the multiple layer construction

-5-

provides an opportunity to vary the conductor particle loading and/or semiconductor particle loading in each layer, such that the outer layers contain lower particle loadings than the inner layer, in order to achieve a wide range of clamping voltages and other desired properties. In an additional aspect of this invention, the outer layer in contact with the electrical conductor of the electronic device should have a lower particle loading than the inner layer with a higher particle loading, but in such case the other outer layer in contact with the ground plane can be higher or lower in particle loading. In an additional aspect of this invention, this multi-layer variable voltage protection component can further be provided with a thin layer of the neat dielectric polymer, glass or ceramic as referred to above on one outside surface or both outside surfaces, in order to provide additional properties and characteristics of the component. In this aspect of the invention, the layer on the side of the electrical conductor can have a higher or lower particle loading than the inner layer provided the neat dielectric polymer, glass or ceramic layer is positioned between the outer layer and the electrical conductor. In another aspect of this invention this multiple layer component can be provided with a conductive, e.g., metal, layer interposed between the first layer and second layer and/or between the second layer and third layer of variable voltage protection material. In yet another aspect of this invention, these multiple layer components themselves can be stacked, with or without the outer layers of neat dielectric polymer, glass or ceramic layers, and with or without an intervening layer of neat dielectric polymer, glass or ceramic between components to achieve desired performance characteristics.

In another aspect, this invention provides a method of making a variable voltage protection material comprising forming a mixture comprising (a) conductive, semiconductive and/or insulative particles and (b) colloidal insulating particles in (c) a light organic solvent; mixing said mixture to disperse the colloidal insulating particles in the

-6-

conductive/ semiconductive/insulative particles; evaporating at least a portion, preferably all, of the solvent; and mixing the resultant mixture of conductive/semiconductive/insulative particles and colloidal insulating particles with a binder to form a variable voltage protection material.

Brief Description of the Drawings

Figure 1 is a cross-section view of an illustration of a variable voltage protection device incorporating a layer of neat dielectric polymer, glass or ceramic.

10 Figure 2 is a cross-section view of an illustration of a variable voltage protection compound having a layer of variable voltage material comprising a binder and conductive particles, semiconductive particles and/or insulative particles in combination with a layer of neat dielectric polymer, glass or ceramic.

15 Figure 3 is a cross section view of an illustration of a multi-layer variable voltage protection component according to this invention and incorporating optional exterior layer of neat dielectric polymer, glass or ceramic.

20 Figure 4 is a cross-section view of an illustration of a multiple layer variable voltage protection component according to this invention incorporating optional interposed metal layers between the layers of variable voltage protection material.

Detailed Description of the Invention

25 Referring to the first aspect of this invention which comprises a variable voltage protection device comprising as the variable voltage protection material a thin layer of a neat dielectric polymer, glass or ceramic, it has been found that such a device is surprisingly effective at a desired range of clamping voltages provided that the layer of neat dielectric polymer, glass or ceramic is sufficiently thin. For some

-7-

polymers a layer of less than about 0.0203 mm (0.8 mil) will provide effective overvoltage protection under various conditions, while for other polymers a layer of less than about 0.0406 mm (1.6 mils) provides the desired performance characteristics. It is preferable in many variable voltage protection applications that the polymer layer be less than about 0.0127 mm (0.5 mil) and more preferably less than about 0.0051 mm (0.2 mil). Similarly, when the layer is a glass or ceramic, it is preferred that the layer be less than about 0.0203 mm (0.8 mil), but for some glasses in certain applications a thickness of up to about 0.0965 mm (3.8 mils) is appropriate. As will be appreciated by one skilled in the art, the actual thickness of the neat dielectric polymer, glass or ceramic layer employed in a particular variable voltage protection function will vary depending on the type of polymer, glass or ceramic used, its dielectric properties, the operating conditions of the device in which the variable voltage protection element is employed and the performance properties required of the protection device.

Fig. 1 illustrates the device of this invention where layer 12 is positioned between electrical conductors 10 and ground plane 14.

As used in the disclosure and description of the present invention, the term "neat dielectric polymer, glass or ceramic" refers to a polymeric, glass or ceramic material which can act as a dielectric or insulating material under the normal voltage and current conditions of intended use and which is unfilled, i.e., does not contain conductive or semiconductive particles such as those typically used in binders or otherwise associated with variable voltage protection materials of the prior art. However, "neat dielectric polymer, glass or ceramic" is intended to include polymeric, glass or ceramic materials which fulfill the above criteria, but which may contain or have added to them insulative or inert particles or materials that are inactive or do not interfere with the desired dielectric/variable voltage protection

-8-

properties of the polymer, glass or ceramic layer as used in the present invention. The polymer, glass or ceramic layer useful in the present invention can be formed or cured in situ or can be provided in a preformed or procured sheet or film and placed in position for use according to this invention. Additionally, the polymer layer can be a pre-cured polymer block from which sheets or layers of polymer can be sliced or shaved in the desired thickness. Further, the polymer, glass or ceramic layer can be provided in the form of a mat of polymer, glass or ceramic fibers or particles which are compressed or otherwise treated to provide the polymer, glass or ceramic layer in the desired thickness and properties for use in this invention. Such a mat, which may contain an adhesive or binder for the fibers can be heated or heat treated while compressed to provide a sheet of polymer, glass or ceramic fibers of desired thickness for use in this invention.

15 The polymers, glasses and ceramics useful in this aspect of the invention can be selected from polymers known in the art to be useful as binders in conventional variable voltage protection materials to the extent that such polymers are known to have high resistance to tracking and high resistance to arcing. In addition, other polymers, glasses and ceramics not previously suitable for or used as such binders are also useful in the present invention if they exhibit sufficient dielectric properties, sufficient resistance to tracking and sufficient resistance to arcing under the operating conditions selected for a device according to this invention.

25 In general, the types of dielectric polymers useful in the present invention include silicone rubber and elastomer, natural rubber, organopolysiloxane, polyethylene, polypropylene, polystyrene, poly(methyl methacrylate), polyacrylonitrile, polyacetal, polycarbonate, polyamide, polyester, phenol-formaldehyde resin, epoxy resin, alkyd resin, polyurethane, polyimide, phenoxy resin, polysulfide resin, polyphenylene oxide resin, polyvinyl chloride, fluoropolymer and

-9-

chlorofluoropolymer. These and other useful polymers can be used by themselves or can include various substituent groups and can be mixtures, blends or copolymers thereof, wherein the final polymer is selected in accordance with the criteria described above. A particularly preferred polymer is a conventional and commercially available General Electric "615" silicone, and it is also particularly preferred to cure this polymer for about 15 minutes at about 200°C to obtain properties better suited for use in this invention. In such a preparation, the curable liquid polymer is coated on the desired ground plane to the desired thickness, then cured as indicated. The cured polymer layer is then placed in contact with the electrical conductor(s) of an electronic device to form the variable voltage protection device of this invention. It has been found that this polymer provides good performance in a thickness of about 0.0051 mm (0.2 mil). Another form of polymer useful in this invention is woven or nonwoven polymer fibers compressed into a mat of desired thickness. For example, a polymer fiber material useful in the present invention is a layer of nonwoven aramid (aromatic polyamide) fibers, commercially available as "KEVLAR" or "NOMEX" nonwoven fiber mat from E.I. Du Pont de Nemours & Company. The nonwoven aramid fiber mat of about 0.0406 mm (1.6 mils) has been found to provide good performance when compressed to a thickness of 0.0203 mm (0.8 mils).

The dielectric glass materials useful in this invention are likewise glass materials which have been used as binders in variable voltage materials such as sodium silicate. As with the polymer type material, the glass material can be either coated on or formed in place on the desired substrate, such as the ground plane, or can be preformed in a sheet and assembled between the ground plane and the electrical conductor to form the device of this invention. The dielectric glass, such as a sodium silicate is generally useful in this invention in thicknesses similar to those outlined above for the polymer materials,

-10-

but is also useful in some instances in thicker layers, e.g., up to about 0.127 mm (5 mils), but usually less than about 0.0965 mm (3.8 mils) and preferably less than about 0.0406 mm (1.6 mils). Further, glass fibers can be used to form the dielectric glass layer in accordance with this invention. For example, a fiberglass mat can be compressed to the desired thickness, e.g., about 0.0254 mm (1 mil) or less, to provide the performance characteristics desired for a particular application in which this invention is to be used. As with the polymer fiber mat, a sheet of nonwoven or woven glass fibers can be compressed, with or without an adhesive or binder present, to the desired thickness under heat treatment to provide a result sheet of desired thickness for use in this invention.

The dielectric ceramics useful in this invention are glass-ceramics, devitrified glasses, crystallized glasses, crystalline ceramics, crystalline ceramic composites and diamond. While diamond is not technically a ceramic, it is included here within the definition of "dielectric ceramic" because it possesses the dielectric properties of conventional ceramics which are useful in this invention. Thus, preferred ceramic materials for use in this invention are aluminum oxides and aluminum nitride, crystalline ceramic composites include those which include AlN, Al_2O_3 , Si_3N_4 and TiN. As noted above for glasses, the ceramics can be used in this invention up to about 0.127 mm (5 mils), usually less than about 0.0965 mm (3.8 mils) and preferably less than 0.0406 mm (1.6 mils).

As used herein "glass" is intended to include the amorphous type glasses and "ceramic" is intended to include the crystalline type glasses and ceramics and diamond crystals. In addition to the above methods of assembly, fabrication and use, it will be recognized by one skilled in the art that the layer of glass and ceramic can be applied for use in this invention by various known methods, such as solvent

-11-

deposition, sol-gel coating, sputtering, evaporation, chemical vapor deposition, plasma spraying, anodizing and the like.

As will be appreciated by one skilled in the art, various dielectric polymers, glasses and ceramics can be selected and used in this invention following the teachings contained herein with respect to the thickness that must be maintained for the neat dielectric polymer, glass or ceramic to exhibit the desired clamping voltage and other desired properties. Examples of polymers which can be employed in this invention include those disclosed in U.S. Patent Nos. 4,298,416, 4,483,973, 4,499,234, 4,514,529, 4,523,001, 4,554,338, 4,563,498, 4,580,794, the disclosures of which are incorporated herein by reference. As indicated, other resins may be selected for use in accordance with this invention.

In another aspect of this invention, it has been found that the above described neat dielectric polymer, glass or ceramic layer can be used in combination with a variable voltage material to modify and enhance certain properties and performance characteristics of the variable voltage material. As referred to as part of this invention, the variable voltage material can be a conventional variable voltage material which comprises a binder containing conductive particles and/or semiconductive particles and/or insulative particles mixed with or treated with colloidal insulating particles as disclosed herein. As used in this invention, the variable voltage material may also include other novel, modified and improved variable voltage materials or variable voltage components such as disclosed in this specification and as disclosed in U.S. application Serial No.08/275,947 filed on 14 July 1994. The neat dielectric polymer, glass or ceramic layer which is used in combination with such variable voltage materials or components is placed in contact with one or both surfaces of the variable voltage material or component and can be the same neat

-12-

dielectric polymer, glass or ceramic referred to and described above in this application.

Fig. 2 illustrates the device of this invention where neat dielectric polymer, glass or ceramic layer 12 is positioned between electrical conductors 10 and variable voltage material 13. Ground plane 14 is provided in contact with layer 13.

In this aspect of the invention, the above-described neat dielectric polymer, glass or ceramic layer can be applied to the surface of a desired variable voltage material or component as described above, for example in a liquid form and cured in place, or can be provided in a pre-cured or pre-formed sheet and laminated to the surface of the variable voltage material or component. It will be recognized by one skilled in the art that various conventional variable voltage materials and components can be combined with the neat dielectric polymer, glass or ceramic layer as described herein to form the combination of this invention, a variable voltage material with an exterior layer of neat dielectric polymer, glass or ceramic, to provide desired performance characteristics. In particular, it is preferred in this aspect of the invention to provide in combination a multi-layer product as described below and a neat dielectric polymer, glass or ceramic layer on one or both exterior surfaces of such a multi-layer variable voltage component.

In another aspect this invention comprises a multi-layer variable voltage protection component which comprises at least three layers of variable voltage material which comprises a binder containing conductive, semiconductive and/or insulative particles and may optionally contain colloidal insulative particles. The multi-layer variable voltage protection component according to this invention comprises two outer layers containing a lower loading or concentration of conductive, semiconductive and/or insulative particles while the inner layer of the component contains a higher loading or concentration of

-13-

conductive, semiconductive and/or insulative particles. As described above, this multi-layer variable voltage protection component can optionally further comprise on either or both surfaces of the component, a neat dielectric polymer, glass or ceramic layer to further enhance or change the performance characteristics as desired.

Fig. 3 illustrates this invention where individual layers of variable voltage protection material 15, 16 and 17 form the multi-layer product positioned between electrical conductors 10 and ground plane 14. Optionally, a neat dielectric polymer, glass or ceramic layer 12 can be positioned on the outside layer 15 and in contact with conductors 10 and/or neat dielectric polymer, glass or ceramic layer 12' can be positioned on the outside of layer 17 and in contact with ground plane 14.

The individual layers of the multi-layer product of this invention can be formulated as conventionally disclosed in the patents referred to in the background section above or more preferably can be formulated and made by the method described herein below. In general, it is preferred that the two outside layers of the present multi-layer product contain at least about 20 percent by volume conductive, semiconductive and/or insulative particles while the inner layer contains at least about 40 percent by volume conductive, semiconductive and/or insulative particles in a binder. It is more preferred that the two outside layers contain at least 30 percent by volume of such particles and the inner layer contains at least about 50 percent and more preferably at least about 60 percent by volume of such particles in the binder. It is not necessary for the two outside layers of the product to contain the same loading or concentration of such particles, for example, one outside layer may contain 30 percent by volume of such particles while the other outside layer contains 40 percent and the inner layer contains 60 percent by volume of such particles in the binder. Following the teachings of this invention, it will

-14-

be apparent to one skilled in the art that the concentrations or loadings of conductive, semiconductive and/or insulative particles in the various layers can be varied to obtain the performance characteristics desired. However, it will further be recognized that the teachings of this

5 invention indicate that the exterior layers of the component contain lower particle loadings than the interior layer or layers. It will further be recognized that the inner or interior layer of this component can itself be made up of multiple layers of variable voltage materials which are higher in particle loading or concentration than the exterior surface
10 layers.

When the first outer layer is in direct contact with the electrical conductor of the electronic device, that outer layer has a lower conductive/semiconductive/insulative particle loading than the inner layer, as outlined above, but the other outer layer is optional and can
15 have a higher or lower particle loading than the inner layer. When the first outer layer comprises a layer of neat dielectric polymer, glass or ceramic which is in contact with the electrical conductor, then the first outer layer can have a higher or lower particle loading than the inner layer and the other outer layer is optional and can have a higher or
20 lower particle loading than the inner layer.

The thickness of each layer and the overall thickness of the multi-layer component can be determined by one skilled in the art following the present disclosure to achieve the desired performance characteristics of the component. For example, a preferred
25 embodiment comprises a first layer of 0.0254 mm (1.0 mil) containing 30 percent by volume of conductive particles, with an inner layer of 0.0203 mm (0.8 mil) containing 60 percent by volume of conductive particles and a third layer of 0.0178 mm (0.7 mil) containing 30 percent by volume of conductive particles. Similarly, another preferred
30 embodiment comprises a first layer of 0.0254 mm (1.0 mil) of 30 percent by volume conductive particles, an inner layer of 0.0508 mm

-15-

(2 mils) of 60 percent by volume conductive particles and a third layer of 0.0203 mm (0.8 mil) of 30 percent by volume conductive particles. Multi-layer configurations such as these provide good performance characteristics. In addition, it will be recognized by one skilled in the art that each layer which is provided in the form of a polymeric or other dielectric binder containing the desired conductive, semiconductive, insulative and/or colloidal insulative particles contained therein can be applied in a liquid form and then dried or cured. The multi-layer product of this invention can be formed by applying two or more of the layers and then curing or drying all of the layers simultaneously or, alternatively, the multi-layer product of this invention can be formed by applying the first layer, for example, to a metal ground plane member, and curing or drying that layer before applying the subsequent layers. In this fashion, each layer can be applied and cured or dried to the desired thickness before the subsequent layer is applied. Thus, it will be recognized by one skilled in the art that the multi-layer variable voltage protection component according to this invention can be formed in various ways using various materials. However, a preferred embodiment is provided by employing the method described herein below for preparing the variable voltage protection material then forming the above multi-layer product of this invention in the particle loadings and the layer thicknesses as described above. It will further be recognized by one skilled in the art that each individual layer can be selected as desired such that each of the layers of the multi-layer product may be of a different type of binder materials and/or conductive, semiconductive, insulative, or colloidal insulative particles provided that the basic criteria is followed in that the exterior layers of the multi-layer product contain the lower concentration or loading of such particles while the interior layer contains a higher loading of such particles. For example, each layer can be selected from the various conventional variable voltage

-16-

materials available in the prior art which comprise a binder containing various conductive and/or semiconductive and/or insulative particles. Alternatively, it will be recognized that each layer can be individually selected to employ the novel and improved variable voltage protection materials or components as disclosed herein or in U.S. application Serial No. 08/275,947 filed on 14 July 1994. In this regard, the novel variable voltage materials containing, for example, the reinforcing mats as disclosed in said co-pending application, can be selected for use as particular individual layers in the multi-layer product of this invention.

10 The multi-layer product of this invention can be constructed such that each layer comprises a binder, such as a dielectric polymer or dielectric glass binder, containing conductive particles, such as aluminum particles, and optionally containing semiconductor particles, such as silicone carbide, and further, optionally containing insulative particles, such as aluminum oxide and/or colloidal insulative particles such as a fumed silica. Each of these various components are well known in the art as well as methods for forming the variable voltage materials with the binders and curing or drying the binders to form the desired final material. In this regard, the disclosures of the above-referenced patents are incorporated herein as providing the basic materials and components which can be used to make the multi-layer product according to the present invention.

25 For use in this invention "conductive particles" include metal particles, such as copper, aluminum, molybdenum, and the like or other conductive materials such as carbon black, carbonyl nickel, tantalum carbide, and the like. "Semiconductive particles" include silicon carbide, beryllium carbide, calcium oxide, and the like. "Insulative particles" include aluminum oxide, glass spheres, calcium carbonate, barium sulphate, and the like. "Colloidal insulative particles" include the colloidal form of fumed silica, kaolin, kaolinite, aluminum trihydrate, feld spar, and the like. Reference is made to U.S. Patent No.

-17-

4,726,991 for further examples of specific particles and materials in each category which are useful in this invention following the procedures and teachings set forth herein.

Fig. 4 illustrates this invention where individual layers of variable voltage protection material 15, 16 and 17 are separated by optional metal layers 18 and 18', which together comprise the multi-layer variable voltage protection device positioned between electrical conductors 10 and ground plane 14.

In another aspect, this invention comprises an improved method of making a variable voltage protection material containing a binder and conductive particles and/or semiconductive particles in combination with insulative particles and colloidal insulative particles all dispersed in the binder. As mentioned above, each of these components of binder, conductive particles, semiconductive particles, insulative particles and colloidal insulative particles are known in the art and are described in various detail in the patents referenced above. The present aspect of this invention involves novel methods of combining these conventional materials to produce novel variable voltage protection materials having enhanced properties. The methods of the present invention comprise a step of dispersing the conductive and/or insulative particles and the desired amount of colloidal insulative particles in an organic solvent whereby the conductive/insulative particles and the colloidal insulative particles are thoroughly dispersed in the solvent mixture. The particles can be added to the solvent in any desired order, but it is generally preferred to disperse the conductive and/or insulative particles in the solvent first, then add the colloidal insulative particles. The mixture is then dried by removing the solvent by evaporation. The dried mixture of particles is usually in the form of a cake, which is then ground to a powder in a grinder. The resulting powder is then added to a dielectric polymer binder in a milling process to uniformly disperse the particles throughout the dielectric polymer. For example, the conductive particle

-18-

can be aluminum, the insulative particle aluminum oxide, the colloidal insulative particle fumed silica and the solvent methyl ethyl ketone. In some formulations it is preferred to also include glass fibers as additional insulative particles. In a preferred aspect, the method

5 further comprises forming a first solvent mixture of just conductive particles and colloidal insulative particles, and forming a second solvent mixture of insulative particles and colloidal insulated particles. Both mixtures are separately dried; the resulting two dry mixtures are separately ground then added simultaneously to a mill to be mixed in a

10 polymer binder to form a desired variable voltage protection material.

In a preferred method, the binder-particle mixture is mixed with an excess of a strong polar solvent, such as MEK, to swell the binder. This mixture is then mixed in a high speed mixer to form a viscous material similar to a pigmented paint. This final mixture can be applied

15 as desired to form variable voltage protection components or layers by depositing the material as desired in layers of desired thickness and allowing the solvent to evaporate and allowing the binder to further cure leaving the desired layer of variable voltage protection material.

In a preferred formulation, STI Dow Corning fluorosilicone rubber

20 (DC-LS2840) is used in combination with a STI Dow Corning polydimethylsiloxane (HA2) in a volume ration of about 4:1. This mixture is milled until it becomes uniform and essentially translucent. At that point, a mixture prepared of aluminum oxide and fumed silica particles is added to the mill. The preparation of the mixture of

25 aluminum oxide particles and fumed silica particles is as follows. A preferred aluminum oxide particle is a 5 micron "A14" particle from Alcoa. This particle is dispersed in methyl alcohol and the particle-solvent mixture passed through a 10 micron screen. To the resulting solvent dispersion of aluminum oxide particles is added 1% by weight

30 (based on the initial weight of the aluminum oxide) of a fumed silica

-19-

particle, which is "Cabosil TS530" predispersed in methyl alcohol and mixed until evenly dispersed through the solvent mixture. The solvent is then removed through evaporation to form a cake. The dried aluminum oxide particle-Cabosil cake is then ground to a powder. A

5 second solvent mixture of an aluminum particle designated "H10" from Alcoa, which is 10 micron particle, likewise dispersed in methyl alcohol then mixed with 17% by weight of a fumed silica, which is "Cabosil M5". As above, the H10 aluminum particles are dispersed in the methyl alcohol and screened through a 20 micron screen, then the

10 Cabosil M5 dispersed in methyl alcohol is added to the screened H10 aluminum particles in the solvent. After mixing the solvent is evaporated to form a cake. The dried aluminum particle-Cabosil cake is then ground to a powder. The ratio of aluminum particles to aluminum oxide particles is about 2:1 and about 45 parts by volume of particles

15 are mixed with about 55 parts by volume of binder. Both the aluminum and the aluminum oxide powders are added to the mill and milled into the polymer mixture. After milling for a sufficient time, such as 30 minutes to an hour, to obtain uniform mixing, the mixture is removed from the mill and mixed with methylethylketone solvent in a weight

20 ratio of about one part solvent per part of total mix from the mill. This mixture is allowed to stand for a period of a few hours, such as overnight, in the MEK, then is mixed with a small amount such as, for example about 4% by weight of a peroxide, which is 1,1-di-t-butylperoxy-3,3,5-trimethyl cyclohexane, and 17% by weight of a

25 crosslinking agent, which is triallylisocyanurate, wherein the weight percent is based on weight of binder. This final mixture is then mixed at low speed to assure thorough mixing then is mixed at high speed until the mixture becomes the consistency of a pigmented paint. This final variable voltage protection composition can then be coated or

30 deposited on a ground plane or on electrical conductors or other substrates in desired patterns, the solvents are allowed to dry and the

-20-

binder allowed to further cure or crosslink. If desired, a temperature of about 200°C for about 20 minutes can be used to assist in the drying and curing or crosslinking of the binder. The variable voltage protection material is thereby provided in the desired thickness and configuration to serve as the variable voltage protection layer or component. This composition can be used to form the multi-layer product invention disclosed above or in combination with the neat dielectric polymer, glass or ceramic layer invention disclosed above.

As used in the above method aspect of this invention the organic solvent can be any solvent in which the desired particles will disperse and mix with other particles. In general the solvent can be a C₁ to C₁₀ hydrocarbon which is substituted or unsubstituted, and include straight and branch chain hydrocarbons, alcohols, aldehydes, ketones, aromatics, and the like. Examples of such solvents useful in this invention include methyl alcohol, ethyl alcohol, n- or iso-propyl alcohol, formaldehyde, methylethyl ketone, toluene, benzene, butane, pentane, the chloro/fluoro ethylenes ("Freon" solvents from Du Pont), and others. It will be recognized by one skilled in the art that a solvent that can be readily evaporated under available conditions is desirable.

As used in the above invention the conductive particles, semiconductive particles and insulative particles are conventional as set forth in the above patents incorporated by reference.

The principles, preferred embodiments and modes of operation of the present invention have been described in the foregoing specification. However, the invention which is intended to be protected is not to be construed as limited to the particular embodiments disclosed. Further, the embodiments described herein are to be regarded as illustrative rather than restrictive. Variations and changes may be made by others, and equivalents employed without departing from the spirit of the present invention, and it is expressly intended that all such variations, changes and equivalents which fall

-21-

**within the spirit and scope of the present invention as defined in the
claims be embraced thereby.**

-22-

WHAT IS CLAIMED IS:

1. A variable voltage protection device comprising:
a ground plane;
a layer of neat dielectric polymer, glass or ceramic in contact
5 with one surface of the ground plane; and
at least one electrical conductor of an electronic device in
contact with said layer of neat dielectric polymer, glass or ceramic;
characterized by said layer being positioned between and in contact
with the ground plane and said electrical conductor and consisting
10 essentially of a layer of neat dielectric polymer having a thickness of
less than about 0.0406 mm (1.6 mils) or consisting essentially of a
layer of neat dielectric glass or ceramic having a thickness of less than
about 0.127 mm (5 mils).
2. A device according to Claim 1 wherein the polymer layer is less
15 than about 0.0203 mm (0.8 mil) and the glass or ceramic layer is less
than about 0.0965 mm (3.8 mils).
3. A device according to Claim 1 wherein the polymer layer is less
than about 0.0127 mm (0.5 mil) and the glass or ceramic layer is less
than about 0.0203 mm (0.8 mil).
- 20 4. A device according to Claim 1 wherein the polymer layer is less
than about 0.0051 mm (0.2 mil) and the glass or ceramic layer is less
than about 0.0127 mm (0.5 mil).
5. A variable voltage protection component for placement between
a ground plane and an electronic circuit comprising:
25 a layer of variable voltage material comprising a binder
containing conductive particles or semiconductive particles; and

-23-

a layer of neat dielectric polymer, glass or ceramic in contact with one surface of said layer of variable voltage material; characterized by the neat dielectric polymer layer having a thickness of less than about 0.0406 mm (1.6 mils) or by the neat dielectric glass or ceramic layer having a thickness of less than about 0.127 mm (5 mils).

6. A variable voltage protection component for placement between a ground plane and an electronic circuit comprising:

a first layer of variable voltage protection material comprising a binder having dispersed therein at least about 20% by volume of conductive or semiconductive particles;

a second layer of variable voltage protection material in contact with the first layer comprising a binder having dispersed therein at least 40% by volume of conductive or semiconductive particles; and

a third layer of variable voltage protection material in contact with said second layer comprising a binder having dispersed therein at least 20% by volume of conductive or semiconductive particles.

7. A component according to Claim 6 wherein the volume percent in the three layers comprise at least about 30%, at least about 40% and at least about 30% respectively.

8. The component according to Claim 6 wherein the volume percent in the three layers comprise at least about 30%, at least about 60% and at least about 30%, respectively.

9. A variable voltage protection component for placement between a ground plane and an electronic circuit comprising:

a first layer of variable voltage protection material which is in direct contact with an electrical conductor in said electronic circuit and

-24-

comprises a binder having dispersed therein at least about 20% by volume of conductive or semiconductive particles; and

5 a second layer of variable voltage protection material in contact with the first layer comprising a binder having dispersed therein at least 40% by volume of conductive or semiconductive particles.

10. A variable voltage protection component according to Claim 9 further comprising a third layer of variable voltage protection material in contact with said second layer comprising a binder having dispersed therein conductive or semiconductive particles at a % by volume which
10 is different than the second layer.

11. A variable voltage protection component for placement between a ground plane and an electronic circuit comprising:

15 a layer of neat dielectric polymer, glass or ceramic which is in direct contact with an electrical conductor in said electronic circuit;

a first layer of variable voltage protection material in contact with said layer of neat dielectric polymer, glass or ceramic and comprises a binder having dispersed therein at least about 20% by volume of conductive or semiconductive particles; and

20 a second layer of variable voltage protection material in contact with the first layer of variable voltage protection material comprising a binder having dispersed therein conductive or semiconductive particles at a % by volume which is different than in said first layer.

12. A variable voltage protection component according to Claim 11 further comprising a third layer of variable voltage protection material
25 in contact with said second layer comprising a binder having dispersed therein conductive or semiconductive particles at a % by volume which is different than the second layer.

-25-

13. A method of making a variable voltage protection material comprising:
- forming a mixture comprising conductive particles and colloidal insulative particles in a light organic solvent;
- 5 mixing said mixture to disperse the colloidal insulative particles in the conductive particles;
- evaporating at least a portion of the solvent; and
- mixing the resultant mixture of conductive particles and colloidal insulative particles with a binder to form a variable voltage protection
- 10 material.
14. A method according to Claim 13 comprising:
- sieving the conductive particles and solvent before evaporating the solvent.
15. A method according to Claim 13 comprising:
- 15 evaporating sufficient solvent to form a cake of the conductive particles and colloidal insulative particles; and
- grinding the cake to form the resultant mixture of particles for mixing with the binder.
16. A method according to Claim 13 comprising:
- 20 forming a separate mixture comprising insulative particles and colloidal insulative particles in a light organic solvent;
- mixing said mixture to disperse the colloidal insulative particles in the insulating particles;
- evaporating at least a portion of the solvent; and
- 25 mixing the resultant mixture of conductive particles and colloidal insulative particles and the resultant mixture of insulative particles and colloidal insulating particles with a binder to form a variable voltage protection material.

-26-

17. A variable voltage protection material formed by:
forming a mixture comprising conductive particles and colloidal
insulative particles in a light organic solvent;
mixing said mixture to disperse the colloidal insulative particles
5 in the conductive particles;
evaporating at least a portion of the solvent; and
mixing the resultant mixture of conductive particles and colloidal
insulative particles with a binder to form a variable voltage protection
material.
- 10 18. A variable voltage protection material formed by:
forming a mixture comprising conductive particles and colloidal
insulative particles in a light organic solvent;
mixing said mixture to disperse the colloidal insulative particles
in the conductive particles;
15 sieving the mixture of particles and solvent;
evaporating sufficient solvent to form a cake;
grinding the cake to form a mixture of conductive particles and
colloidal insulative particles; and
mixing the resultant mixture of conductive particles and colloidal
20 insulative particles with a binder to form a variable voltage protection
material.
19. A variable voltage protection material formed by:
forming a first mixture comprising conductive particles and
colloidal insulative particles in a light organic solvent;
25 mixing said first mixture to disperse the colloidal insulative
particles in the conductive particles;
evaporating at least a portion of the solvent from the first
mixture;

-27-

forming a second mixture comprising insulative particles and colloidal insulative particles in a light organic solvent;

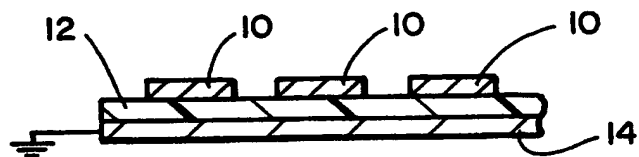
mixing said second mixture to disperse the colloidal insulating particles in the insulative particles;

5 evaporating at least a portion of the solvent from the second mixture; and

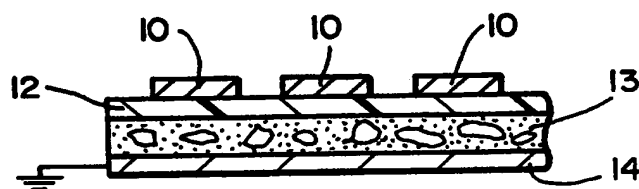
10 mixing the resultant first mixture of conductive particles and colloidal insulative particles and the resultant second mixture of insulative particles and colloidal insulative particles with a binder to form a variable voltage protection material.

20. A variable voltage protection composition comprising a mixture of a binder, a mixture of conductive particles and fumed silica and a mixture of insulative particles and fumed silica.

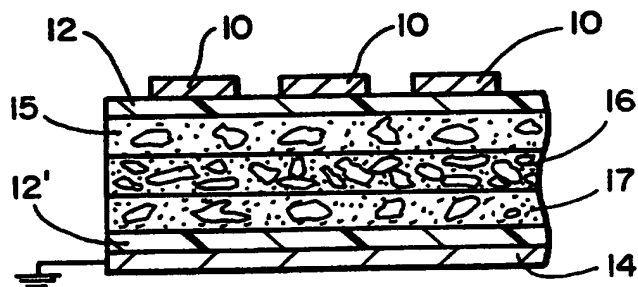
1/1



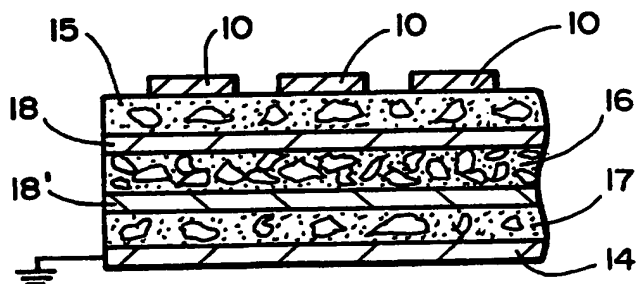
FIG_1



FIG_2



FIG_3



FIG_4

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 95/08808

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6 H01C7/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 H01C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US,A,5 183 698 (STEPHENSON ROGER C ET AL) 2 February 1993 see column 4, line 49 - column 5, line 19; figures 2,3 ---	1
A	EP,A,0 487 920 (ASEA BROWN BOVERI) 3 June 1992 see figure 3 ---	6-8
A	EP,A,0 220 003 (RAYCHEM CORP) 29 April 1987 see figure 1 ---	6
A	PATENT ABSTRACTS OF JAPAN vol. 006 no. 139 (C-116), 28 July 1982 & JP,A,57 063365 (CHUGOKU TORYO KK) 16 April 1982, see abstract ---	13-20
-/-		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "A" document member of the same patent family

Date of the actual completion of the international search

21 November 1995

Date of mailing of the international search report

29.11.95

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Lina, F

INTERNATIONAL SEARCH REPORT

Intern: 1 Application No
PCT/US 95/08808

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	PATENT ABSTRACTS OF JAPAN vol. 012 no. 391 (C-537) ,18 October 1988 & JP,A,63 137972 (JAPAN SYNTHETIC RUBBER CO LTD) 9 June 1988, see abstract ----	13-20
A	US,A,4 977 357 (SHRIER KAREN P) 11 December 1990 cited in the application see the whole document ----	1,6,9, 11,13
A	US,A,4 928 199 (DIAZ STEPHEN H ET AL) 22 May 1990 cited in the application see the whole document ----	1,6,9,11
A	US,A,5 246 388 (COLLINS CHRISTOPHER J ET AL) 21 September 1993 cited in the application see the whole document ----	1,6,9,11
A	US,A,5 248 517 (SHRIER KAREN P ET AL) 28 September 1993 cited in the application see the whole document ----	1,6,9,11
A	US,A,5 189 387 (CHILDERS RICHARD K ET AL) 23 February 1993 cited in the application see the whole document -----	1,6,9,11

INTERNATIONAL SEARCH REPORT

information on patent family members

Internat'l Application No

PCT/US 95/08808

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A-5183698	02-02-93	NONE	
EP-A-0487920	03-06-92	SE-B- 467513 CA-A- 2054487 JP-A- 4266001 SE-A- 9003448 US-A- 5382938 SE-A- 9003814	27-07-92 01-05-92 22-09-92 01-05-92 17-01-95 31-05-92
EP-A-0220003	29-04-87	US-A- 4743321 AU-B- 594379 AU-B- 6350686 CA-A- 1262467 JP-A- 62093902	10-05-88 08-03-90 09-04-87 24-10-89 30-04-87
US-A-4977357	11-12-90	AU-B- 3042489 EP-A- 0362308 JP-T- 2503049 WO-A- 8906859 US-A- 5068634	11-08-89 11-04-90 20-09-90 27-07-89 26-11-91
US-A-4928199	22-05-90	AU-B- 584998 AU-B- 5536486 EP-A, B 0196891 JP-A- 61259559	08-06-89 02-10-86 08-10-86 17-11-86
US-A-5246388	21-09-93	EP-A- 0577311 JP-A- 6208869	05-01-94 26-07-94
US-A-5248517	28-09-93	AU-A- 3136393 WO-A- 9309882	15-06-93 27-05-93
US-A-5189387	23-02-93	NONE	

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☐ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.